

MACROS: Molecular Analyzer for Complex Refractory Organic-rich Surfaces S. A. Getty¹, X. Li², W. B. Brinckerhoff¹, J. E. Elsila¹, A. Grubisic³, T. Cornish⁴, M. Balvin¹, A. Southard⁵, and J. Ferrance⁶, ¹NASA Goddard Space Flight Center (8800 Greenbelt Road, Mailstop 699, Greenbelt, MD 20771; Stephanie.A.Getty@nasa.gov), ²University of Maryland, Baltimore County (1000 Hilltop Cir, Baltimore, MD 21250), ³University of Maryland, College Park (College Park, MD), ⁴C&E Research, Inc. (Columbia, MD), ⁵Universities Space Research Association (Greenbelt, MD), ⁶J2F Engineering (Charlottesville, VA).

Introduction: The objectives of future landed missions to solar system destinations of high astrochemical and astrobiological interest will require science instrumentation capable of conducting broad, comprehensive, and highly sensitive *in situ* analyses of surface materials. A primary goal of any such landed mission will be a detailed characterization of the local chemical environment. The Molecular Analyzer for Complex Refractory Organic-Rich Surfaces (MACROS; Figure 1) addresses the limitations of predecessor instrument technologies, namely the propensity of indigenous salts and oxidants to confound the detection and identification of trace organics in an acquired surface sample with state-of-the-art flight instrumentation. MACROS goes several steps beyond current spaceflight analytical capabilities to integrate laser desorption/ionization mass spectrometry (LDMS) [1,2] with *in situ* solvent extraction and liquid-phase analysis using liquid chromatography (LC) [3]. This integration will achieve unprecedented capabilities within a compact instrument footprint, compatible with a Discovery or New Frontiers mission to high-priority targets, including Europa, Enceladus, Titan, Mars, a comet, or a carbonaceous asteroid.

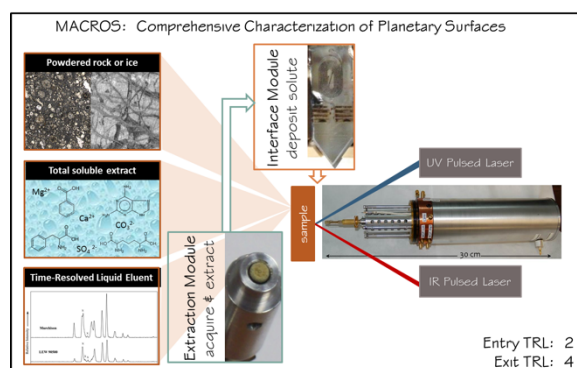


Figure 1. Instrument concept of MACROS, in which analysis of a native unprepared sample is then compared to the solvent-extracted fraction and chromatographically separated eluents.

Instrument Concept: MACROS combines drill and sample acquisition development, solvent-based sample extraction, and liquid deposition interfaced to laser desorption/ionization (LDI).

Drill and Sample Acquisition Development: A 1.5 mm ID diamond coring drill, as shown in Figure 2, can be used as both a means to collect ground powdered specimens from rock surfaces, as well as to provide a sample holder that can be interfaced directly to the ion source of a miniature time-of-flight mass spectrometer (TOF-MS) for LDMS broad survey mode. For an airless body, no vacuum interface between the sample and TOF-MS will be required. The drill further provides an internal volume to capture rock powder for extraction in the MACROS solvent extraction module. To realize this additional capability, current testing is focused on characterizing the powdered mineral sample accumulated in the drill under various conditions, including as a function of sample hardness and drill dimensions.

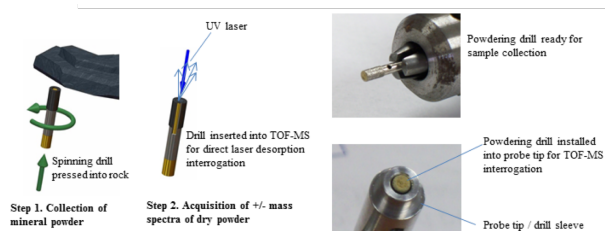


Figure 2: A potential design of drill bit that will have the capabilities to both present drilled fines to the LDMS for survey mode, and also contain extraction solvent and deliver the extracted sample to the fluidic components of MACROS.

Sample Extraction: We tested various solvent extraction procedures using a variety of analog samples, including powdered Allende meteorite, Green River Shale, and samples from the Painted Desert. Two different solvent systems were used: isopropanol:water (50:50, targeting polar compounds) and dichloromethane (DCM, which targets non-polar compounds). DCM also extracts elemental sulfur, which can dominate the LDMS spectrum, so a simple sulfur removal step was added to our procedure using a copper surface.

Extract Interface Module Development: MACROS is designed to analyze the composition of solvent-extracted sample for detailed analysis of the soluble organic fraction of a planetary sample. This component of the instrument is intended to be compatible with

liquid chromatography but does not rely on separation to accomplish the baseline objectives of the MACROS development. The interface module enables an interface between the liquid eluent from the extraction module to a vacuum region necessary for MS analysis. We have demonstrated spray desposition from a number of geometries and nozzle dimensions to deposit liquid analyte onto a secondary LDI substrate. This element enables several compelling analytical capabilities: (1) enrichment of total soluble extract through controlled deposition duration, (2) front-end coupling to an ion exchange column or solid phase extraction component for desalting and purification, and (3) time-resolved mass analysis of chromatographically resolved eluent.

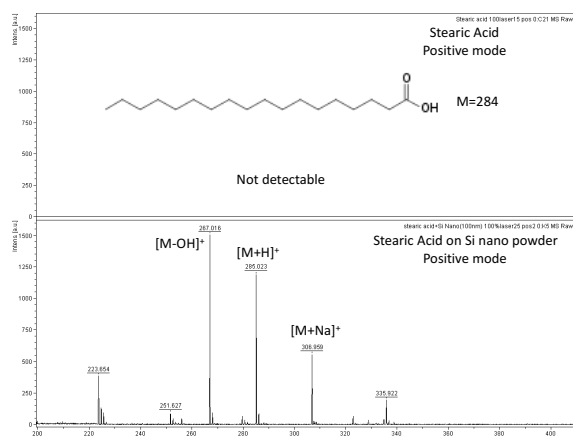


Figure 3. Enhanced detection of stearic acid is seen for a silicon nanoparticle iMALDI underlayer.

To increase the detection sensitivity of organics, particularly those that are difficult to detect by LDI alone, in the deposited liquid extracts, a substrate covered with thin matrix layer is used. In traditional matrix-assisted LDI (MALDI), an organic acid (or “matrix”) is used to promote the ionization of intact large organic molecules during the MS analysis. However, organic matrix is not well suited to a robotic flight configuration given the complexity of the required sample preparation and the risk for cross- and forward-contamination with terrestrial organics. As an alternative path, the development of inorganic matrix-assisted laser desorption/ionization (iMALDI) has now been demonstrated allowing the detection of a broader suite of organic composition. A series of inorganic micro-particle and nanoparticle chemistries have been investigated for their effectiveness in promoting the desorption and ionization process with a 266 nm ultraviolet (UV) laser. Likewise, the optimal choice for iMALDI matrix will impart minimal background signal to the mass spectra obtained with MACROS. Evaluating the

trade between sensitivity and background signal, we have selected the silicon nanoparticles for pursuant sample analyses, and one example enhancement is shown in Figure 3 for stearic acid, a model lipid and key biosignature.

Sample Analysis: MACROS will feature different modes of operation to allow systematic measurements of the broad inorganic and organic composition using LDMS mode (survey mode) [1], the aromatic composition of the sample using L2MS mode (detailed mode) [2] and the soluble inorganic salts at low mass and soluble organics at mid-molecular weights. An comparison between LDMS and L2MS is shown for the Murchison meteorite, using GSFC miniature mass spectrometer prototypes for demonstration of MACROS capabilities (Figure 4). Improved sensitivity and selectivity to key classes of organics, as in L2MS, can be used to differentiate between structural isomers that appear at the same nominal mass in an organically complex sample.

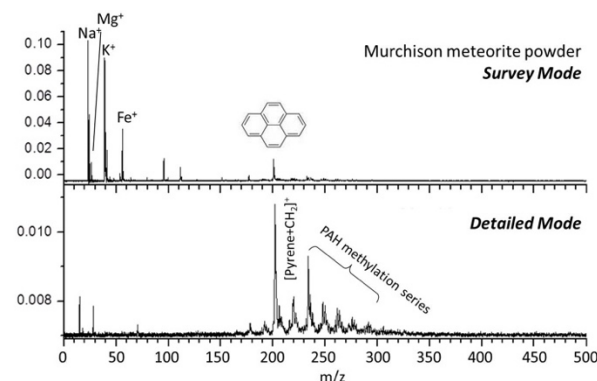


Figure 4: Sample Analysis of Murchison meteorite under LDI survey mode and detailed mode.

Conclusion: MACROS is a hybrid LC/LDMS instrument that will provide sophisticated sample analysis beyond the capabilities of either technique alone. This new instrument package can be used to determine inorganic mineral composition, broadband organic sample content, and detailed structural analysis of high-priority compound classes for a thorough understanding of the chemistry of planetary surface materials.

References: [1] Li X. et al. (2015) *IEEE Aerospace Conference*. [2] Getty S. A. et al. (2012) *Rapid Communications in Mass Spectrometry*, 26, 1. [3] Getty S. A. et al. (2013) *IEEE Aerospace Conference*.